Lecture 34

Equilibrium Conditions for Charged Species

Last Time

Reactions with Condensed Phases

Ellingham Diagrams: Oxidation

Electrochemistry

Background:
Consider the maximum work that can be obtained when 1 mole of of hydrogen combines with half a mole of of oxygen to form water vapor at 25°C.

\[
\begin{align*}
H_2(gas) + \frac{1}{2}O_2(gas) & \rightleftharpoons H_2O(gas) \\
\Delta H_{Rx}(T = 300^\circ K, P = 1\text{atm}) & = 286\text{(KJ/(moleH}_2) \\
\Delta S_{Rx}(T = 300^\circ K, P = 1\text{atm}) & = [70 - (130.5 + \frac{1}{2}205)] = -163\text{(J/(moleH}_2^\circ K))
\end{align*}
\]

The entropy of the thermal surroundings of the reaction increase by

\[
\Delta S_{\text{surround}}(T = 300^\circ K, P = 1\text{atm}) = \frac{286 \times 10^3}{300} = 953\text{(J/(moleH}_2^\circ K))
\]

So the total entropy of the universe increases\(^\text{34}\) by 953 – 163 = 790 \frac{J}{\text{mole}^\circ K}.

\textbf{WHAT a WASTE!} In order \textbf{not} to violate the second law, only only \(q_{\text{min}}\) amount of heat needs to be transferred.

\(^{34}\)It had better increase because we know this is spontaneous reaction.
\[
\frac{\Delta S_{\text{surround.}}}{T_{\text{surround.}}} + \Delta S_{R_x} = 0 \quad \text{reversible}
\]

\[
\frac{q_{\text{min}}}{T_{\text{surround.}}} = \frac{q_{\text{min}}}{300} = -\Delta S_{R_x} = 163 \text{J/(moleH}_2\text{K)}
\]

which leaves
\[
\Delta H - q_{\text{min}} = w_{\text{max}}
\]

\[
w_{\text{max}} = \Delta H - (-\Delta S)T = \Delta G
\]

\[
= 286 \times 10^3 - (163)(300) = 237 \text{J/(moleH}_2\text{)}
\]

Apparently, \(\Delta G^{rx}\) represents the maximum work that can be extracted from a system.

How can this work be extracted? In principle it could be harnessed to drive an electric motor. To do this, a source of electrons is needed and those can be generated by the reactions:

\[
\text{H}_2(\text{gas}) \rightleftharpoons 2\text{H}^+(\text{Aq.}) + 2e^- \quad \text{(generates electrons)}
\]

\[
\frac{1}{2}\text{O}_2(\text{gas}) + 2\text{H}^+(\text{Aq.}) + 2e^- \rightleftharpoons \text{H}_2\text{O(liqu.)} \quad \text{(consumes electrons)}
\]

The work done by the electric motor is the potential drop between the source and sink of the electrons, multiplied by the net charge that they carry:

\[
w_{\text{max}} \text{ (done by system)} = \Delta \phi(2N_{\text{avg.}}|e|)
\]

\[
-\Delta G_{R_x} = \Delta \phi_{\text{max}} 2F
\]

or

\[
\Delta \phi_{\text{max}} = -\frac{\Delta G_{R_x}}{n_iF}
\]

The maximum potential is related to the molar Gibbs free energy of the reaction.

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**Systematic Treatment of the Electrochemical Potential**

Recall how the the internal degrees of freedom were extended to include work terms associated with the transfer of charged particles from one electrostatic potential to another:

\[
dU = TdS - PdV + \sum_{i=1}^{C} \mu_i dn_i + \sum_{i=1}^{C} \Delta \phi_i Z_i F dn_i
\]

(Note: \(dn_i\) represents the change in the number of moles of species \(i\) if \(\mu_i\) is the chemical potential of a mole of species \(i\). This is done so that the Faraday constant \(F\) appears in the equation from the start—the Faraday constant is the charge on a mole of electrons.)

Equation 34-8 can be rewritten as
\[ dU = TdS - PdV + \sum_{i=1}^{C} (\mu_i + \Delta \phi_i Z_i F) dn_i \]  

(34-9)

\[ dU = TdS - PdV + \sum_{i=1}^{C} \eta_i dn_i \]

where

\[ \eta_i dn_i \equiv \mu_i + \Delta \phi_i Z_i F \]  

(34-10)

\[ \eta_i \] is called the “electrochemical potential”.

The conditions for equilibrium are analogous to all other reactions:

\[ \sum_{i=1}^{C} \eta_i dn_i = 0 \quad \text{subject to} \quad \sum_{i=1}^{C} dn_i = 0 \]  

(34-11)

and when, in addition, the system is closed (\( \sum dN_i = 0 \))

\[ \eta^\alpha_i = \eta^\beta_i \quad \text{or} \quad (\mu^\alpha_i + \phi^\alpha_i Z_i F) + (\mu^\beta_i + \phi^\beta_i Z_i F) \]  

(34-12)

### An Example

![Example Battery Diagram](image)

Figure 34-1: Example Battery

Writing out the equilibrium equations between each of the phases:
At I/II

\[ \eta_I^{\text{Cu}^{++}} = \eta_{II}^{\text{Cu}^{++}} \]

\[ \mu_I^{\text{Cu}^{++}} + 2F \phi_I = \mu_{II}^{\text{Cu}^{++}} + 2F \phi_{II} \]  

(34-13)

At II/III

\[ \mu_{\text{SO}_4^{--}}^{II} - 2F \phi_{II} = \mu_{\text{SO}_4^{--}}^{III} - 2F \phi_{III} \]  

(34-14)

At III/IV

\[ \mu_{\text{Zn}^{++}}^{III} + 2F \phi_{III} = \mu_{\text{Zn}^{++}}^{IV} + 2F \phi_{IV} \]  

(34-15)

At Electrodes

\[ \text{Cu} \rightleftharpoons \text{Cu}^{++}_{(\text{aq.})} + 2e^- \quad \text{and} \quad \text{Zn} \rightleftharpoons \text{Zn}^{++}_{(\text{aq.})} + 2e^- \]  

(34-16)

or

\[ \mu_{\text{Cu}}^{I} = \mu_{\text{Cu}^{++}}^{I} + 2\mu_{e}^{-} \quad \text{and} \quad \mu_{\text{Zn}}^{II} = \mu_{\text{Zn}^{++}}^{II} + 2\mu_{e}^{-} \]  

(34-17)

Combining all the equilibrium equations and solving:

\[ \phi_I - \phi_{IV} = \frac{1}{2F} \left[ (\mu_{IV}^{\text{Zn}} - \mu_{III}^{\text{Zn}^{++}}) - (\mu_{I}^{\text{Cu}} - \mu_{II}^{\text{Cu}^{++}}) + (\mu_{II}^{\text{SO}_4^{--}} - \mu_{III}^{\text{SO}_4^{--}}) \right] \]  

(34-18)

If the membrane is perfect: \( \mu_{\text{SO}_4^{--}}^{II} = \mu_{\text{SO}_4^{--}}^{III} \), then:

\[ \Delta \phi = \frac{1}{nF} \left[ \frac{G_I^{Rx}}{G_{II}^{Rx}} + RT \log \frac{a_{\text{Zn}^{++}}}{a_{\text{Cu}^{++}}} \right] \]  

(34-19)

Which is known as the Nernst Equation.

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\(^{35}\)The difference in chemical potentials of electrons in two different materials at the same voltage is the difference in Fermi levels.